

## PATENT ABSTRACTS OF JAPAN

(11) Publication number :

2001-354836

(43) Date of publication of application : 25.12.2001

(51) Int.Cl.

C08L 63/00  
 C08G 59/24  
 C08K 3/36  
 C08K 5/5399  
 C08L 21/00

(21) Application number : 2000-177676

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(22) Date of filing : 14.06.2000

(72) Inventor : SAITO SEIICHI

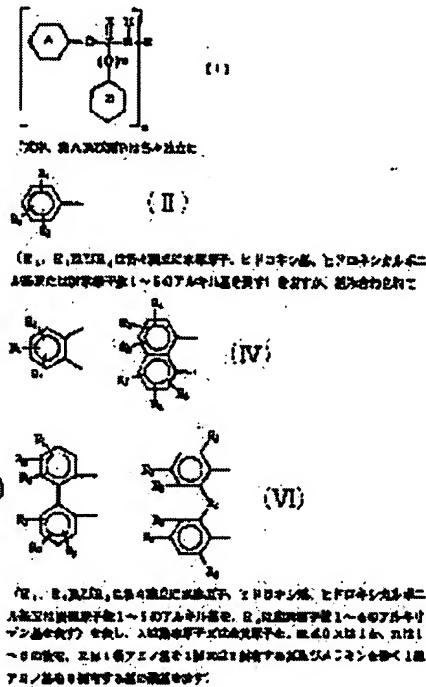
MORI TAKAHIRO

## (54) FLAME RETARDANT EPOXY RESIN COMPOSITION

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain an epoxy resin composition capable of exhibiting good flame retardance without containing a halogen and excellent in mechanical strength, etc.

SOLUTION: This flame retardant epoxy resin composition is obtained by adding a phosphoric acid amide compound represented by the following general formula (I) [wherein, rings A and B denote each independently formula (II) (wherein, R1, R2 and R3 denote each independently hydrogen atom, hydroxy group, hydroxycarbonyl group or a 1-5C alkyl group) or in combination denote formula (III), (IV), (V) or (VI) (wherein, R1/R2 and R3 denote each independently hydrogen atom, hydroxy group, hydroxycarbonyl group or a 1-5C alkyl group; and R4 denotes a 1-4C alkylidene group); X denotes oxygen atom or sulfur atom; m denotes 0 or 1; n denotes a number of 1-3; and R denotes a group having 1 or 2 primary amino groups and a residue of a group having 3 primary amino groups except melamine].



10.60

spec. p. 14, Flame retardant 2

14.91

11.65

c1.7

foaming agent

cl. 7

15

XLC-LL

p. 13, Curing agent B

6/12/07

AN 2001:932557 CAPLUS  
DN 136:54631  
ED Entered STN: 27 Dec 2001  
TI Halogen-free epoxy resin compositions fireproofed by phosphoric amides  
IN Saito, Seiichi; Mori, Takahiro  
PA Asahi Denka Kogyo K. K., Japan  
SO Jpn. Kokai Tokkyo Koho, 16 pp.  
CODEN: JKXXAF

DT Patent  
LA Japanese  
IC ICM C08L063-00  
ICS C08G059-24; C08K003-36; C08K005-5399; C08L021-00  
CC 37-6 (Plastics Manufacture and Processing)  
Section cross-reference(s): 38, 76

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001354836	A	20011225	JP 2000-177676	20000614 <--
PRAI	JP 2000-177676		20000614		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 2001354836	ICM	C08L063-00
	ICS	C08G059-24; C08K003-36; C08K005-5399; C08L021-00
	IPCI	C08L0063-00 [ICM, 7]; C08G0059-24 [ICS, 7]; C08G0059-00 [ICS, 7, C*]; C08K0003-36 [ICS, 7]; C08K0003-00 [ICS, 7, C*]; C08K0005-5399 [ICS, 7]; C08K0005-00 [ICS, 7, C*]; C08L0021-00 [ICS, 7]
	IPCR	C08L0063-00 [I, C*]; C08L0063-00 [I, A]; C08G0059-00 [I, C*]; C08G0059-24 [I, A]; C08K0003-00 [I, C*]; C08K0003-36 [I, A]; C08K0005-00 [I, C*]; C08K0005-5399 [I, A]; C08L0021-00 [I, C*]; C08L0021-00 [I, A]

OS MARPAT 136:54631  
GI

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB The compns., possessing high Tg and offering moldings with high mech. strength, contain phosphoric amides represented by (i) I [A, B = R1R2R3C6H2 (R1-3 = H, OH, hydroxycarbonyl, C1-5 alkyl) or o-phenylene, Q1, Q2, or Q3 (R4 = C1-4 alkylidene) as combined form; X = O, S; m = 0, 1; n = 1-3; R = 1-3-primary amino-bearing group excluding melamine], (ii) (R1R2R3C6H2O)2P(:O)NHR5C6H4(ZC6H4)1R6NHP(:O)(OC6H2R1R2R3)2 (R1-3 = the same definition as above; R5, R6 = single bond, C1-4 alkylene; Z = single bond, O, S, sulfonyl, ester, amide, C1-4 alkylidene, condensed ring; l = 0, 1), or (iii) Q2P(:O)NHCH2C6H4CH2NHP(:O)Q2 (Q = phenoxy). The compns. further containing silica, rubber, and novolak-type hardeners are also claimed. The compns. are useful for prepgs. (Thus) a composition of bisphenol A epoxy resin 40, carboxylated NBR-bisphenol A diglycidyl ether adduct 20, 2,2-bis(3,4-epoxycyclohexyl)propane 40, II 40, XLC-LL (benzene-formaldehyde-phenol condensate) 18.8, PR 53194 (phenolic novolak) 18.8, ethylene glycol Bu ether acetate 80, 2E4MZ 3.5 parts offered a cured product showing Tg 179°, tensile strength 85 MPa, elongation 13%, and UL 94 fire resistance rating V0.

ST phosphoric amide fireproofed epoxy resin compn; nonhalogen epoxy compn novolak hardener flame retardancy; circuit board prepreg nonhalogen epoxy resin fireproofed

IT Nitrile rubber, properties

RL: POF (Polymer in formulation); PRP (Properties); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
(carboxylated, reaction products with bisphenol A diglycidyl ether;

phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT Phenolic resins, properties  
RL: MOA (Modifier or additive use); PRP (Properties); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
(novolak, epoxy resin hardeners; phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT Fire-resistant materials  
Fireproofing agents  
(phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT Epoxy resins, properties  
RL: POF (Polymer in formulation); PRP (Properties); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
(phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT 7631-86-9, Silica, properties  
RL: MOA (Modifier or additive use); PRP (Properties); USES (Uses)  
(fillers; phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT 3848-51-9P  
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)  
(fireproofing agents; phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT 470-87-1 382596-14-7 382596-15-8 382596-16-9 382596-17-0  
RL: MOA (Modifier or additive use); PRP (Properties); USES (Uses)  
(fireproofing agents; phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT 26834-02-6, XLC-LL 50830-44-9, Benzene-formaldehyde-phenol copolymer  
119792-27-7, Sumilite PR 53194  
RL: MOA (Modifier or additive use); PRP (Properties); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
(hardeners; phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT 1477-55-0, 1,3-Bis(aminomethyl)benzene 2524-64-3  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(in preparation of sp. phosphoric amides as fireproofing agents for epoxy resin compns.)

IT 9003-18-3  
RL: POF (Polymer in formulation); PRP (Properties); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
(nitrile rubber, carboxylated, reaction products with bisphenol A diglycidyl ether; phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

IT 1675-54-3D, Bisphenol A diglycidyl ether, reaction products with carboxylated NBR 14513-43-0, 2,2-Bis(3,4-epoxycyclohexyl)propane,  
25068-38-6, Bisphenol A epoxy resin  
RL: POF (Polymer in formulation); PRP (Properties); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
(phosphoric amide-fireproofed halogen-free epoxy resin compns. showing good mech. strength)

DERWENT-ACC-NO: 2002-274930

DERWENT-WEEK: 200266

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TITLE: Halogenfree flame retardant epoxy resin composition useful in the preparation of copper lined laminates and printed circuit boards, contains phosphoric acid amide compound

PATENT-ASSIGNEE: ASAHI DENKA KOGYO KK[ASAE]

PRIORITY-DATA: 2000JP-0177676 (June 14, 2000)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN IPC
<u>JP 2001354836 A</u>	December 25, 2001	N/A	016	C08L 063/00

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2001354836A	N/A	2000JP0177676	June 14, 2000

INT-CL (IPC): C08G059/24, C08K003/36, C08K005/5399, C08L021/00, C08L063/00

ABSTRACTED-PUB-NO: JP2001354836A

BASIC-ABSTRACT:

NOVELTY - A flame-retardant epoxy resin composition contains a phosphoric acid amide compound.

DETAILED DESCRIPTION - A flame-retardant epoxy resin composition contains a phosphoric acid amide compound of formula (1).

ring A, ring B = group of formula (Ia) or a combination of formula (Ib), (Ic), (Id) or (Ie);

R1, R2, R3 = H, OH, hydroxycarbonyl or 1-5C alkyl;

R4 = 1-4C alkylidene;

X = O or S atom;

m = 0 or 1;

n = 1-3; and

R = group having 1 or 2 primary amino group(s) or 3 primary amino groups, except for melamine.

USE - The resin composition is suitable for preprg which is useful for preparing copper-lined laminates or a printed circuit board.

ADVANTAGE - The resin composition is free from halogen and has good flame resistance, high glass transition point and good mechanical strength.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: HALOGEN FREE FLAME RETARD EPOXY RESIN COMPOSITION USEFUL PREPARATION COPPER LINING LAMINATE PRINT CIRCUIT BOARD CONTAIN PHOSPHORIC ACID AMIDE COMPOUND

## \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the epoxy resin constituent by which flameproofing was carried out with the reactant phosphoric-acid amide compound.

#### [0002]

[Description of the Prior Art] In recent years, in addition to fire retardancy, about the epoxy resin product, a demand called fewer harmful nature and higher safety is growing with the rise of the interest about safety to a global environmental problem and the body. That is, an epoxy resin product not only cannot burn easily, but it is requested that there is little generating of harmful nature gas or emitting smoke. Conventionally, generally the bromination epoxy resin which contains the bromine which acts as a flame retarder as the flameproofing approach of the epoxy resin used for a casting article, a coating, adhesives, a printed circuit board, etc., especially the tetrabromobisphenol A mold epoxy resin are used.

[0003] Although such a bromination epoxy resin has good fire retardancy, since it generates hydrogen halide (hydrogen bromide) gas harmful at the time of combustion, the use is being controlled. Therefore, the constituent which blended a non-halogen series flame retardant, for example, a nitride, phosphorus compounds, an inorganic compound, etc. with the usual epoxy resin is developed. However, these fire retardancy grant nature additive has a bad influence on hardening of an epoxy resin, or has the problem of reducing the moisture resistance of a hardening constituent.

[0004] For example, although using a reactant phosphoric ester compound was proposed by JP,10-195178,A, since it becomes, or a part became the three-dimensional structure, the viscosity of an epoxy resin increased that it will be easy to absorb moisture if phosphoric ester is incorporated into resin and workability fell greatly, it was not practical.

[0005] Moreover, it is proposed by JP,8-12692,A that the phosphoric-acid amide compound of a melamine is useful as a flame retarder. However, in the epoxy resin, it functioned as a cross linking agent, and the hardened material obtained had a scarce problem in flexibility.

[0006] Furthermore, the nonresponsive phosphoric-acid amide compound is proposed by JP,10-175985,A. This compound is nonresponsiveness and resin physical properties are reduced in a low-molecular-weight object existing in resin.

[0007] In addition, the phosphonic acid amide is proposed by JP,6-212067,A. However, it may be a proposal as a flame retarder for polyester resin, itself may be the amount of macromolecules, and the engine performance is insufficient as a flame retarder of an epoxy resin.

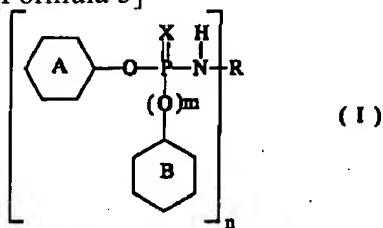
[0008] Therefore, this invention was not made in order to cancel the above-mentioned fault, and it aims at offering the epoxy resin constituent excellent in mechanical strength etc. while it shows fire retardancy good [ without including a halogen ].

#### [0009]

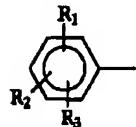
[Means for Solving the Problem] The constituent mentioned later finds out attaining the above-mentioned purpose, and this invention persons complete this invention, as a result of repeating research wholeheartedly in view of the above-mentioned present condition.

[0010] That is, this invention offers the fire-resistant epoxy resin constituent which had the phosphoric-acid amide compound expressed with the following general formula (I) in the first place added.

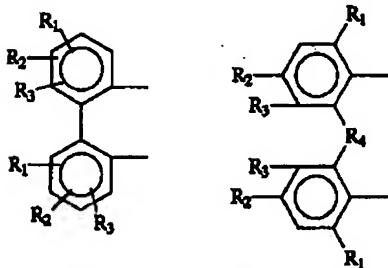
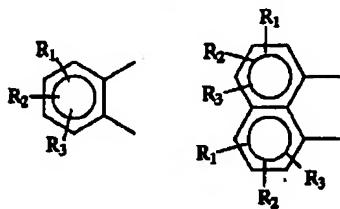
[Formula 5]



[式中、環A及び環Bは各々独立に



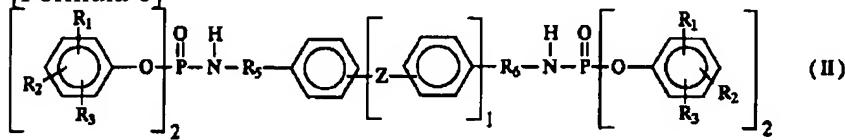
(R<sub>1</sub>、R<sub>2</sub>及びR<sub>3</sub>は各々独立に水素原子、ヒドロキシ基、ヒドロキシカルボニル基または炭素原子数1～5のアルキル基を表す)を表すか、組み合わされて



(R<sub>1</sub>、R<sub>2</sub>及びR<sub>3</sub>は各々独立に水素原子、ヒドロキシ基、ヒドロキシカルボニル基又は炭素原子数1～5のアルキル基を、R<sub>4</sub>は炭素原子数1～4のアルキリデン基を表す)を表し、Xは酸素原子又は硫黄原子を、mは0又は1を、nは1～3の数を、Rは1級アミノ基を1個又は2個有する基及びメラミンを除く1級アミノ基を3個有する基の残基を表す)

[0011] The second is provided with the above-mentioned fire-resistant epoxy resin constituent excellent in the machine physical properties whose above-mentioned phosphoric-acid amide compound is a compound expressed with the following general formula (II), and fire retardancy.

[Formula 6]

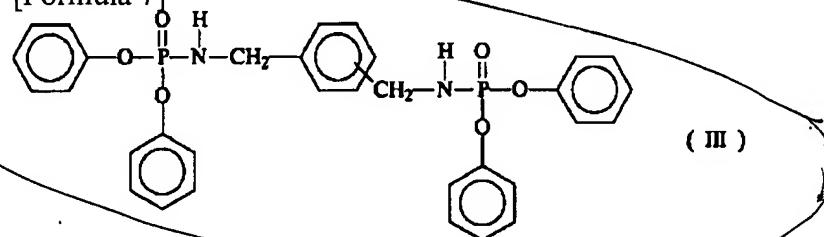


(R1, R2, and R3 -- each -- independent -- a hydrogen atom, a hydroxy group, a hydroxy carbonyl group, or the alkyl group of the carbon atomic numbers 1-5 -- R5 and R6 -- each -- independently, Z expresses the alkylidene radical of direct coupling, an oxygen atom, a sulfur atom, a sulfonyl group, an ester bond, amide association, and the carbon atomic numbers 1-4, or the condensation of a ring, and I expresses the

number of 0 or 1 for the alkylene group of direct coupling or the carbon atomic numbers 1-4)

[0012] The third is provided with the above-mentioned fire-resistant epoxy resin constituent excellent in especially machine physical properties and fire retardancy whose above-mentioned phosphoric-acid, amide compound is the following compound (III).

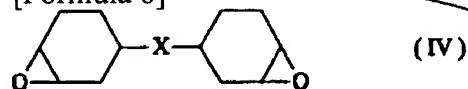
[Formula 7]



( III )

[0013] The above-mentioned fire-resistant epoxy resin constituent which has a high glass transition temperature containing the compound in which an epoxy resin is shown [ fourth ] by the following general formula (IV) is offered.

[Formula 8]



( IV )

(Y expresses the alkylene group or alkylidene radical of the carbon atomic numbers 1-8 among a formula)

[0014] The above-mentioned fire-resistant epoxy resin constituent which is excellent in the mechanical strength which had a silica, rubber, and a phenol novolak mold-curing agent fifth added is offered.

[0015]

[Embodiment of the Invention] Hereafter, this invention is explained in detail.

[0016] It sets at a ceremony (I) and is R1, R2, and R3. As an alkyl group expressed, methyl, ethyl, propyl, isopropyl, butyl, the second butyl, tertiary butyl, pentyl, etc. are mentioned.

[0017] It sets at a ceremony (I) and is R4. Methylene, ethylidene, propylidene, butylidene, etc. are mentioned as an alkylidene radical expressed.

[0018] In a formula (I), aromatic amines, such as aryl alkylamine; anilines [, such as ethylamine, propylamine, and a butylamine /, such as alkylamine; cyclohexylamine, /, such as cycloalkyl amine; benzylamine, ], 2, and 6-dimethylaniline, etc. are mentioned as an amino compound which gives the organic residue which has the one 1st class amino group expressed with R. In addition, the compound which has epoxy groups other than amines, such as an aminophenol and an aminobenzoic acid, and the functional group which reacts is mentioned, since it can add as a curing agent, the compound of these 2 organic functions is easy to blend, and it is desirable.

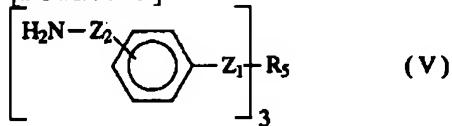
[0019] As an amino compound which gives the organic residue which has the two 1st class amino groups expressed with R in a formula (I) For example, alkylene diamines, such as ethylenediamine and a hexamethylenediamine; Diethylenetriamine, Polyalkylene polyamine, such as triethylenetetramine and tetraethylenepentamine; Isophorone diamine, 1, 3-diamino methylcyclohexane, bis(3-methyl-4-amino cyclohexyl) methane, A 1-amino-1-methyl-4-(2-amino-2-methylethyl) cyclohexane, Aliphatic series diamine which has cycloalkyl radicals, such as a screw (4-amino cyclohexyl methane); polypropylene oxide - alpha, omega-diamine, The aliphatic series diamine compound which has ether linkage, such as 1, the 9-screw (3-aminopropyl) -2, 4 and 8, and 10-tetraoxaspiro undecane; P-phenylene diamine, m-phenylenediamine, bis(4-aminophenyl) methane, the bis(4-aminophenyl) ether, A bis(4-aminophenyl) sulfoxide, a 4-aminophenyl-4'-aminophenyl amide, Aromatic series diamine compounds, such as 2, 4-diamino-6-phenyl-1,3,5-triazine, 2, and 4-diamino-6-methyl-1,3,5-triazine; 1, 3-bis(aminomethyl) benzene, The aliphatic series diamine compound which has rings, such as 1 and 4-bis(aminomethyl) benzene, is mentioned.

[0020] In a formula (I), the compound expressed with the following general formulas (V) is mentioned,

for example as an amino compound which gives the organic residue which has the three 1st class amino groups except the melamine expressed with R.

[0021]

[Formula 9]

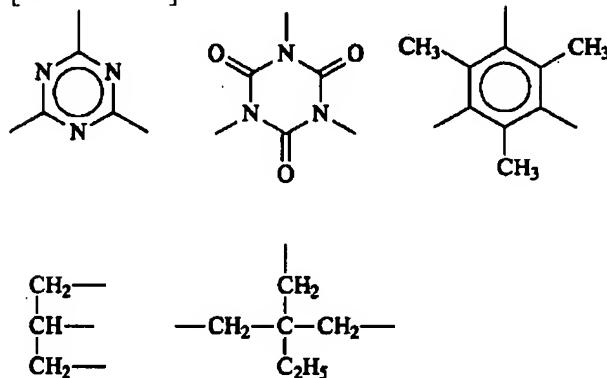


(Z1 and Z2 show an organic radical trivalent in R5 for the alkylene group or alkyleneoxy radical of direct coupling, ether linkage, and the carbon atomic numbers 1-4 independently respectively among a formula)

[0022] R5 As a trivalent organic radical expressed, the following organic radicals are shown, for example.

[0023]

[Formula 10]



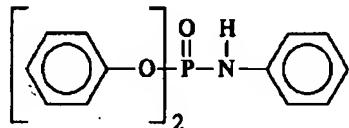
[0024] Z1 And Z2 Methylene, ethylene, a propylene, trimethylene, tetramethylen, etc. are mentioned as an alkylene group expressed, and the radical corresponding to the above-mentioned alkylene group is mentioned as an alkyleneoxy radical.

[0025] More specifically as a compound expressed with the above-mentioned general formula (I), following compound No.1-30 are mentioned. However, this invention is not restricted at all by the following instantiation.

[0026]

[Formula 11]

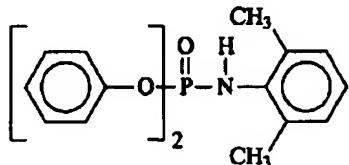
化合物 No.1



[0027]

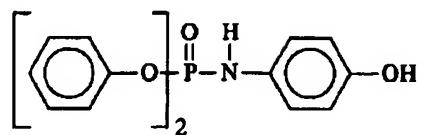
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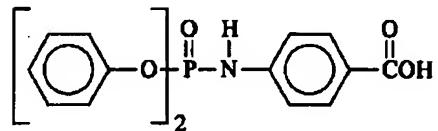


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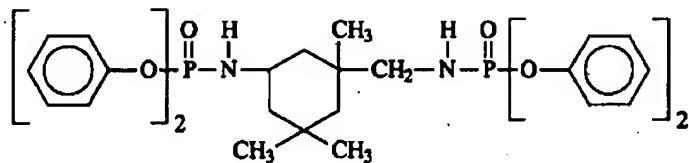
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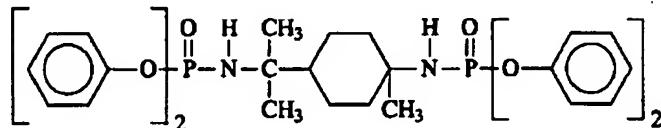
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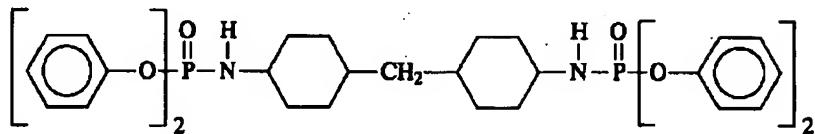
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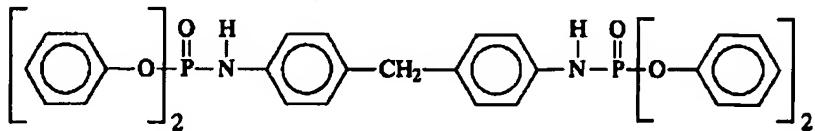
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[0032]  
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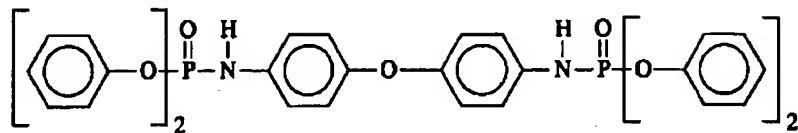


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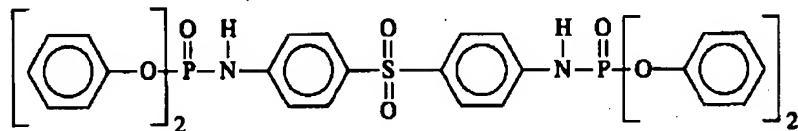


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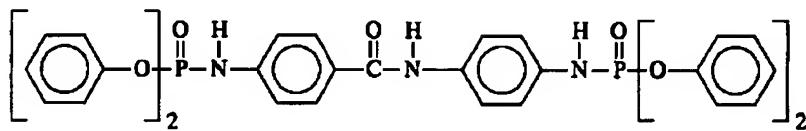
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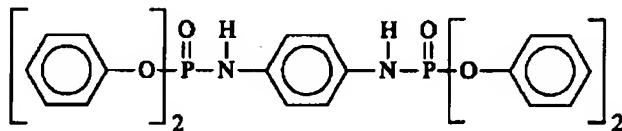
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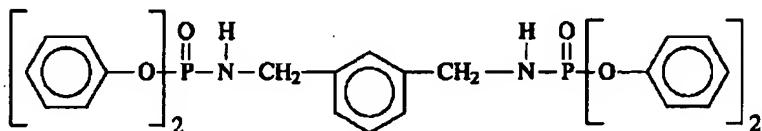
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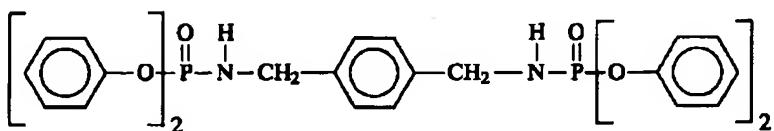
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[0038]  
[Formula 23]  
化合物 No.13



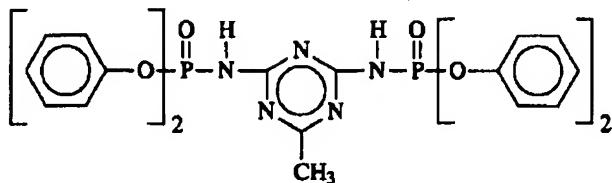
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[0040]

[Formula 25]

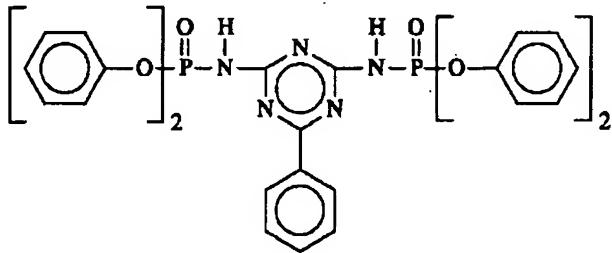
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[0041]

[Formula 26]

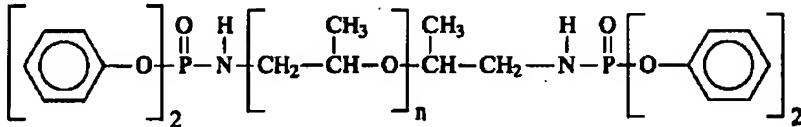
化合物 No.16



[0042]

[Formula 27]

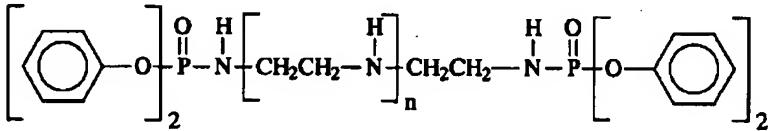
化合物 No.17



[0043]

[Formula 28]

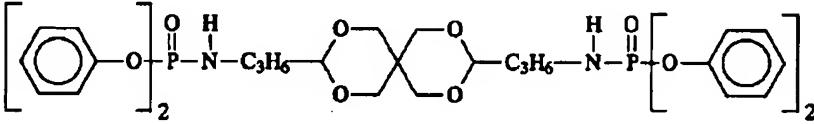
化合物 No.18



[0044]

[Formula 29]

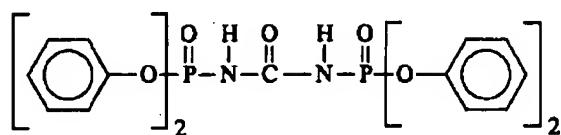
化合物 No.19



[0045]

[Formula 30]

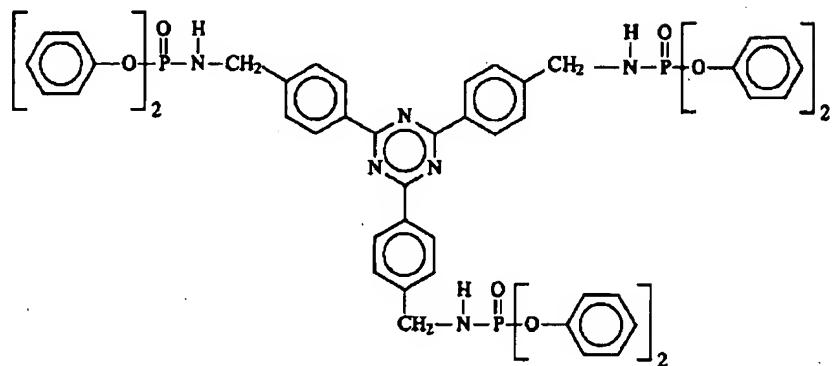
## 化合物 No.20



[0046]

[Formula 31]

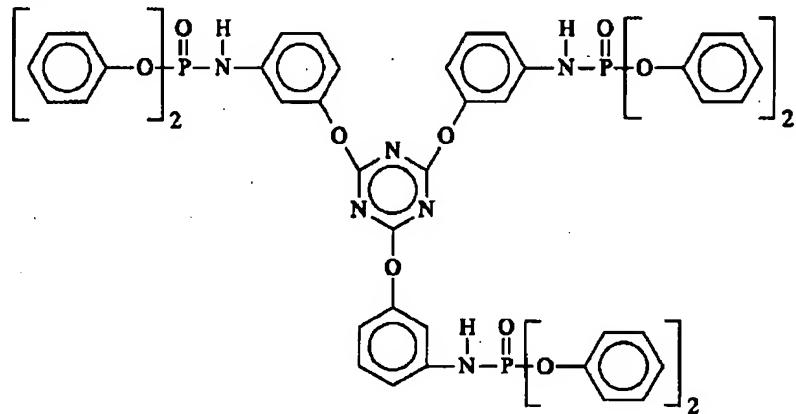
## 化合物 No.21



[0047]

[Formula 32]

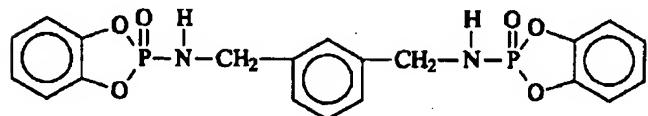
## 化合物 No.22



[0048]

[Formula 33]

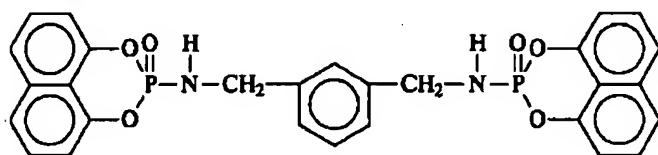
## 化合物 No.23



[0049]

[Formula 34]

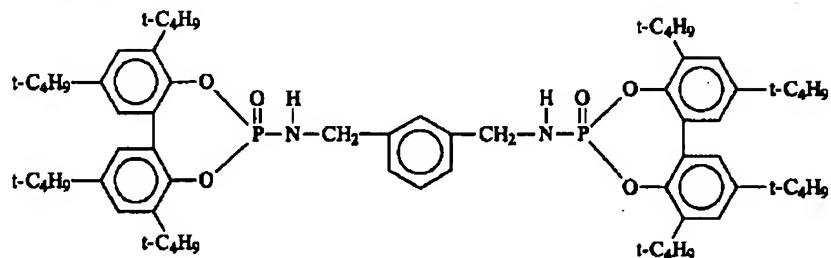
化合物 No.24



[0050]

[Formula 35]

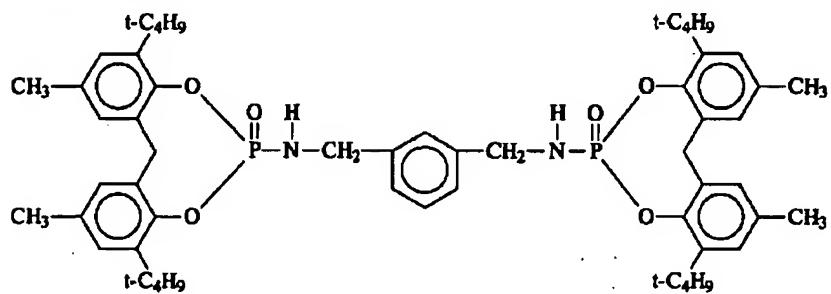
化合物 No.25



[0051]

[Formula 36]

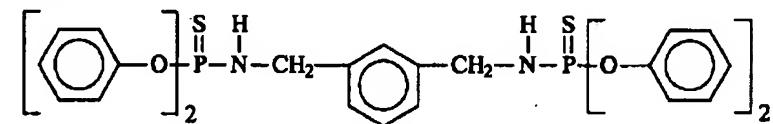
化合物 No.26



[0052]

[Formula 37]

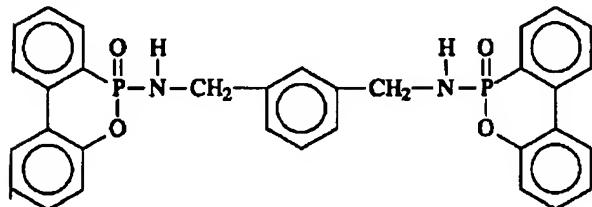
化合物 No.27



[0053]

[Formula 38]

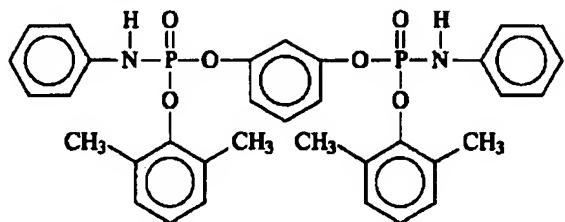
化合物 No.28



[0054]

[Formula 39]

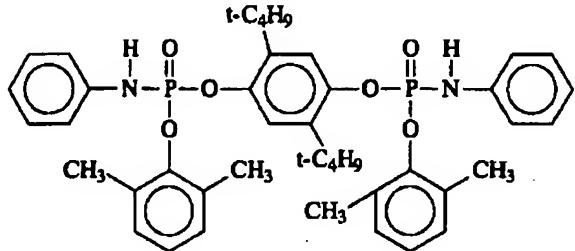
### 化合物 No.29



[0055]

[Formula 40]

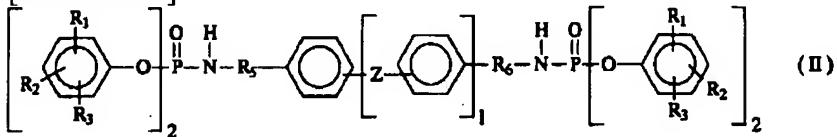
### 化合物 No.30



[0056] Since it can add easily with the loadings of arbitration as a curing agent of an epoxy resin and the compound expressed with the following general formula (II) in the above-mentioned compound is excellent in fire retardancy and mechanical strength, it is desirable.

[0057]

[Formula 41]



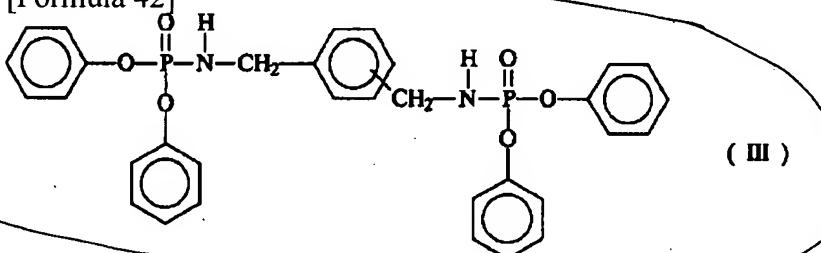
(R1, R2, and R3 -- each -- independent -- a hydrogen atom, a hydroxy group, a hydroxy carbonyl group, or the alkyl group of the carbon atomic numbers 1-5 -- R5 and R6 -- each -- independently, Z expresses the alkylidene radical of direct coupling, an oxygen atom, a sulfur atom, a sulfonyl group, an ester bond, amide association, and the carbon atomic numbers 1-4, or the condensation of a ring, and l expresses the number of 0 or 1 for the alkylene group of direct coupling or the carbon atomic numbers 1-4)

[0058] R5 And R6 As an alkyl group expressed, methyl, ethyl, propyl, isopropyl, butyl, the second butyl, tertiary butyl, etc. are mentioned.

[0059] Especially since the compound expressed with the following general formula (III) in the above-mentioned compound has the good balance of reinforcement and flexibility, it is desirable.

〔0060〕

[Formula 42]



[0061] As the synthetic approach of the above-mentioned compound, it is easily obtained by making phosphorus oxychloride and amine compounds, such as diphenyl phosphoric-acid chloride, react, for

example. Moreover, when facing compounding the compound in this invention and using for electronic parts relation, in order to maintain an electrical property, it is desirable to make a chlorine content low by adsorbent processing, alkali-cleaning processing, rinsing processing, etc.

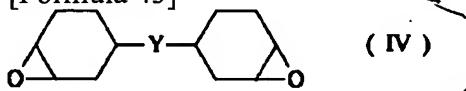
[0062] As an approach of applying the compound expressed with the above-mentioned general formula (I) in this invention to an epoxy resin, the compounds in this invention are an epoxy group and reactivity, and the compound of two organic functions or three organic functions is incorporated by the N-H radical of a phosphoric-acid amide into resin structure as a curing agent and a cross linking agent, and the compound of one organic functions is built into an epoxy resin end, and also you may also incorporate it as an epoxy resin side chain by making it react with a trivalent epoxy compound.

[0063] As an epoxy resin (polyvalent epoxy compound) used for this invention, an aromatic series epoxy compound, an alicycle group epoxy compound, an aliphatic series epoxy compound, etc. are used. As an aromatic series epoxy compound, the glycidyl ether compound of polyhydric phenols, such as a hydroquinone, resorcinol, bisphenol A, Bisphenol F, 4, and 4'-dihydroxy biphenyl, a novolak, and tetrabromobisphenol A, is mentioned, for example. Cyclohexene oxide and the cyclopentene oxide content compound which are obtained by carrying out epoxidation of the poly glycidyl ether or the cyclohexene of polyhydric alcohol which has at least one or more alicyclic rings, or the cyclopentene ring content compound with an oxidizer as an alicycle group epoxy compound are mentioned. For example, hydrogenation bisphenol A diglycidyl ether, 3, 4-epoxycyclohexylmethyl -3, 4-epoxycyclohexylcarboxylate, 3, 4-epoxy-1-methylcyclohexyl -3, 4-epoxy-1-methylhexane carboxylate, The 6-methyl -3, the 4-epoxy cyclo HEKISHI methyl-6-methyl -3, 4-epoxy cyclohexane carboxylate, The 3 and 4-epoxy-3-methylcyclohexyl methyl -3, 4-epoxy-3-methylcyclohexane carboxylate, 3, the 4-epoxy-5-methylcyclohexyl methyl -3, 4-epoxy-5-methylcyclohexane carboxylate, A bis(3, 4-epoxycyclohexylmethyl) horse mackerel peat, methylenebis (3, 4-epoxy cyclohexane), A 2 and 2-bis(3, 4-epoxycyclohexyl) propane, dicyclopentadiene diepoxide, KISHIRU etc. is mentioned to an ethylene screw (3, 4-epoxy cyclohexane carboxylate), epoxy hexahydrophthalic acid dioctyl, and epoxy hexahydrophthalic acid G 2-ethyl. The copolymer compounded as an aliphatic series epoxy compound by the vinyl polymerization of the homopolymer, glycidyl acrylate or glycidyl methacrylate compounded by the vinyl polymerization of aliphatic series polyhydric alcohol or the poly glycidyl ether of the alkylene oxide addition product, the poly glycidyl ester of aliphatic series long-chain polybasic acid, glycidyl acrylate, or glycidyl methacrylate, and other vinyl monomers is mentioned. As a typical compound, 1,4-butanediol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, the triglycidyl ether of a glycerol, The triglycidyl ether of trimethylol propane, the tetraglycidyl ether of a sorbitol, The hexa glycidyl ether of dipentaerythritol, the diglycidyl ether of a polyethylene glycol, The glycidyl ether of polyhydric alcohol, such as diglycidyl ether of a polypropylene glycol, Moreover, the poly glycidyl ether of the polyether polyol obtained by adding one sort or two sorts or more of alkylene oxide to aliphatic series polyhydric alcohol, such as propylene glycol, trimethylol propane, and a glycerol, The diglycidyl ester of an aliphatic series long-chain dibasic acid is mentioned. Furthermore, the monoglycidyl ether of the monoglycidyl ether of aliphatic series higher alcohol, a phenol, cresol, butylphenol, and the polyether alcohol obtained by adding alkylene oxide to these, the glycidyl ester of a higher fatty acid, epoxidized soybean oil, epoxy stearic acid octyl, epoxy butyl stearate, epoxidation polybutadiene, etc. are mentioned.

[0064] Since the hardened material of the epoxy resin obtained is excellent in a water resisting property and softening temperature when the compound expressed with the following general formulas (IV) among the above-mentioned polyvalent epoxy compounds is used, it is desirable.

[0065]

Formula 43



(Y expresses the alkylene group or alkylidene radical of the carbon atomic numbers 1-4 among a

formula)

[0066] As an alkylene group of the carbon atomic numbers 1-4 expressed with Y in a general formula (VI), methylene, ethylene, trimethylene, tetramethylene, etc. are mentioned and ethylidene, propylidene, 2, and 2-propylidene, butylidene, etc. are mentioned as an alkylidene radical.

[0067] As an epoxy resin curing agent, a latency curing agent, polyamine compound, a polyphenol compound, a cation system photoinitiator, etc. are mentioned.

[0068] As a latency curing agent, a dicyandiamide, hydrazide, an imidazole compound, amine adduct, sulfonium salt, onium salt, ketimine, an acid anhydride, the third class amine, etc. are mentioned. These latency curing agent gives a 1 liquid type hardenability constituent, and since it is easy handling, it is desirable.

[0069] As an acid anhydride, a phthalic-acid anhydride, trimellitic anhydride, a pyromellitic acid anhydride, a tetrahydrophthalic anhydride, a hexahydrophthalic anhydride, a maleic-acid anhydride, a succinic-acid anhydride, etc. are mentioned, for example.

[0070] As polyamine compound, for example Ethylenediamine, diethylenetriamine, Aliphatic series polyamine, such as triethylenetetramine, a MENSENJI amine, Isophorone diamine, bis(4-amino-3-methylcyclohexyl) methane, Alicycle group polyamine, such as a bis(aminomethyl) cyclohexane, 3, the 9-screws (3-aminopropyl) 2, 4, and 8, and 10-tetraoxaspiro [5, 5] undecane, The fatty amine, m-phenylenediamine which have rings, such as meta xylene diamine, Aromatic series polyamine, such as 2 and 2-bis(4-aminophenyl) propane; diamino diphenylmethane, diaminodiphenyl sulfone, alpha, and alpha-bis(4-aminophenyl)-p-diisopropylbenzene, is mentioned.

[0071] As a polyphenol compound, a phenol novolak, o-cresol novolak, t-butylphenol novolak, dicyclopentadiene cresol, terpene diphenol, a TERUPENJI catechol, 1 and 1, 3-tris (3-tertiary butyl-4-hydroxy-6-methylphenyl) butane, butylidenebis (3-tertiary butyl-4-hydroxy-6-methylphenyl), etc. are mentioned, for example. Since the electrical property of the epoxy resin obtained and mechanical strength are suitable for the laminate, a phenol novolak is desirable.

[0072] The cation system photoinitiator used for this invention is a compound with possible making the matter which makes cationic polymerization start by energy-line exposure emit, and especially a desirable thing is the double salt which is onium salt which emits Lewis acid by exposure, or its derivative. As a typical thing of this compound, the salt of the cation expressed with following [general formula A]  $m+[B] m-$  and an anion can be mentioned.

[0073] Cation [A]  $m^+$  has that desirable of onium \*\*\*\*\* here, and the structure can be expressed with following general formula [(R19) a Q]  $m^+$ .

[0074] Furthermore, carbon numbers are 1-60 and R19 is the organic radical which may also contain atoms other than a carbon atom how many here. a -- 1-5 -- it is an integer. a R19 is independence respectively; and even if the same, it may differ. Moreover, as for at least one, it is desirable that it is an organic radical like the above which has a ring. Q is the atom chosen from the group which consists of S, N, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, F, and N=N, or an atomic group. Moreover, when the valence of Q in cation [A]  $m^+$  is set to q, it is required to realize the relation it is unrelated  $m=a-q$  (however, N=N is treated as a valence 0).

[0075] Moreover, as for anion [B]  $m^-$ , it is desirable that it is a halogenide complex, and the structure can be expressed for example, with following general formula [LXb]  $m^-$ .

[0076] Furthermore, L is the metal or semimetal (Metalloid) which is the neutral atom of a halogenide complex, and is B, P, As, Sb, Fe, Sn, Bi, aluminum, calcium, In, Ti, Zn, Sc, V, Cr, Mn, Co, etc. here. X is a halogen atom. b -- 3-7 -- it is an integer. Moreover, when the valence of L in anion [B]  $m^-$  is set to p, it is required to realize the relation it is unrelated  $m=b-p$ .

[0077] as the example of anion [LXb]  $m^-$  expressed with the above-mentioned general formula -- tetrafluoroborate (BF<sub>4</sub>) -, hexafluoro phosphate (PF<sub>6</sub>) -, hexafluoroantimonate (SbF<sub>6</sub>) -, hexafluoroarsenate (AsF<sub>6</sub>) -, and hexa chloro antimonate (SbCl<sub>6</sub>) - etc. -- it is mentioned.

[0078] Moreover, the thing of the structure expressed with [LXb-1 (OH)]  $m^-$  can also be preferably used for anion B $m^-$ . L, X, and b are the same as that of the above. Moreover, as an anion which can be used in addition to this, perchloric acid ion (ClO<sub>4</sub>) -, trifluoromethyl sulfite ion (CF<sub>3</sub> SO<sub>3</sub>) -, fluorosulfonic

acid ion (FSO<sub>3</sub>)<sup>-</sup>, a toluenesulfonic acid anion, a trinitro benzenesulfonic acid anion, etc. are mentioned.

[0079] It is effective especially to use the aromatic series onium salt of following I - Ha also in such onium salt in this invention. Out of these, it is independent about one of them, or two or more sorts can be mixed and used.

[0080] b) Aryl diazonium salt, such as phenyl diazonium hexafluorophosphate, 4-methoxyphenyl diazonium hexafluoroantimonate, and 4-methylphenyl diazonium hexafluorophosphate.

[0081] b) Diaryl iodonium salts, such as diphenyliodonium hexafluoroantimonate, JI (4-methylphenyl) iodonium hexafluorophosphate, and JI (4-tert-butylphenyl) iodonium hexafluorophosphate.

[0082] c) Triphenylsulfonium hexafluoroantimonate, tris (4-methoxyphenyl) sulfonium hexafluorophosphate, Diphenyl-4-thio phenoxyphenyl sulfonium hexafluoroantimonate, Diphenyl-4-thio phenoxyphenyl sulfonium hexafluorophosphate, 4 and 4'-bis(diphenyl SURUFONIO) phenylsulfide-screw-hexafluorophosphate, 4 and 4'-screw [JI (beta-hydroxy ethoxy) phenyl SURUHONIO] phenylsulfide-screw-hexafluoroantimonate, 4 and 4'-screw [JI (beta-hydroxy ethoxy) phenyl SURUHONIO] phenylsulfide-screw-hexafluorophosphate, 4-[4'-(benzoyl) phenylthio] phenyl-G (4-fluoro phenyl) sulfonium hexafluoroantimonate, Triarylsulfonium salts, such as 4-[4'-(benzoyl) phenylthio] phenyl-G (4-fluoro phenyl) sulfonium hexafluorophosphate, etc. are desirable.

[0083] In addition to this as a desirable thing, moreover, iron-arene complexes, such as [(eta<sub>5</sub>-2, 4-cyclopentadiene-1-IRU) (1, 2, 3, 4, 5, 6, -eta) - (1-methylethyl) benzene]-iron-hexafluorophosphate, The mixture of aluminum complexes, such as tris (acetylacetone) aluminum, tris (ethyl acetonate) ASETATO) aluminum, and tris (salicyl ARUDEHIDATO) aluminum, and silanols, such as a triphenyl silanol, etc. is mentioned.

[0084] It is desirable to use aromatic series iodonium salt, aromatic series sulfonium salt, and an iron-arene complex from a viewpoint of a practical use side and photosensitivity also in these.

[0085] These photoinitiators may be used combining one sort of well-known photopolymerization accelerators, such as a benzoic-acid system or a tertiary-amine system, or two sorts or more. As for a photoinitiator, it is desirable among the epoxy resin constituent of this invention to contain 0.1 to 30% of the weight. At less than 0.1 % of the weight, when [ than 30 % of the weight ] more [ the addition effectiveness may not be acquired and ], the mechanical strength of a hardened material may fall.

[0086] As the light source used for the polymerization in the case of using a photoinitiator, using the well-known light sources, such as a high pressure mercury vapor lamp, a metal halide lamp, and a xenon lamp, it is emitting Lewis acid from the above-mentioned photoinitiator by the exposure of activity energy lines, such as ultraviolet rays, an electron ray, an X-ray, a radiation, and a RF, and effectiveness of the above-mentioned epoxy compound is carried out. As these light sources, the light source which has the wavelength of 400nm or less is effective.

[0087] In order to improve fire retardancy, as for the fire-resistant epoxy resin constituent of this invention, it is desirable to use a nitrogen-containing compound together. As a nitrogen-containing compound, a melamine and its derivative, cyanuric acid and its derivative, guanamine, its derivative, etc. are mentioned. However, the compound which has the 1st class amino group or the 2nd class amino groups, such as a melamine, is the curing agent of an epoxy resin, and since it influences greatly the physical properties of the epoxy resin which will be obtained if it blends so much stiffening, it is desirable [ a compound ] to use as a derivative according to the physical properties required of an epoxy resin. For example, as a melamine derivative, the phenol resin containing a nitrogen atom etc. is mentioned into the molecule obtained as a copolycondensation resin of a phenolic compound, a melamine compound, and an aldehyde compound. Needless to say, phenol resin can be used as a curing agent of an epoxy resin.

[0088] As for the fire-resistant epoxy resin constituent of this invention, resin other than other hardenability compounds, a hardening accelerator, and an epoxy resin or rubber, a screen-stencil disposition top agent, other flame retarders, a fire-resistant assistant, a bulking agent, a solvent, etc. are added if needed.

[0089] As the above-mentioned hardening accelerator, imidazole compounds, such as triphenyl phosphine, diazabicycloundecen, 2 and 4, 6-tris (dimethyl aminomethyl) phenol and 2-ethyl-4-methylimidazole, and 1-benzyl-2-methylimidazole, are contained. These hardening accelerators are independent, or can be combined two or more sorts and can be used. A hardening accelerator is used in sufficient small quantity to promote hardening of an epoxy resin.

[0090] The rubber which improves the shock resistance excellent in the elasticity of butadiene rubber, nitrile rubber, butadiene-styrene rubber, acrylonitrile-butadiene rubber, acrylonitrile-butadiene-styrene rubber, ethylene-propylene rubber, etc. as rubber used for the fire-resistant epoxy resin constituent of this invention is desirable in respect of mechanical strength.

[0091] The inorganic bulking agent contained in the fire-resistant epoxy resin constituent of this invention is for giving an additional flame retarder, thermal resistance, and moisture resistance to an epoxy resin constituent. Talc, a silica, an alumina, an aluminum hydroxide, a magnesium hydroxide, a glass fiber, etc. can be contained, and it is independent, or two or more sorts can be combined and it can use for these bulking agents. Since it excels in an electrical property, as for a silica, it is desirable to use a silica, when using the epoxy resin constituent of this invention for an electric application.

[0092] The fire-resistant epoxy resin constituent of this invention described above dilutes this with suitable organic solvents, such as propylene glycol monomethyl ether, it can apply a varnish, nothing, and this to porous glass base materials, such as a nonwoven glass fabric and a glass cloth, can be infiltrated, and can manufacture prepreg by the usual method of heating. Moreover, this can be heated on the usual conditions, this prepreg can be pressurized, after laying copper foil on top of one side or both sides of two or more sheet superposition and its laminated structure, and glass epoxy copper clad laminate can be obtained. A laminate is obtained if copper foil is not used at this time. A multilayer board is superposition and this about prepreg and copper foil at least to one side of the inner strake after forming a circuit in copper clad laminate (inner strake) and carrying out etching processing of the copper foil subsequently 170 degrees C and 40kg/cm<sup>2</sup> It can manufacture by the usual method of heating and pressurizing for 90 minutes by the pressure. Furthermore, after a printed wired board forms a through hole in copper clad laminate or a multilayer board and performs through hole plating, it can be manufactured by the usual method of forming a predetermined circuit.

[0093]

[Example] Hereafter, an example explains this invention concretely.

[0094] [A synthetic example]

(Composition of compound No.1) 1 and 3-bis(aminomethyl) benzene 136.2g (one mol) and triethylamine 111.3g (1.1 mols) were dissolved in THF200ml, and 1000ml of THF solutions of diphenyl phosphoric-acid chloride 537.2 (two mols) was dropped below 10 degrees C in 2 hours. It reacted under heating reflux after the reaction at the room temperature for 3 hours for 1 hour. Toluene 300ml was added, the triethylamine hydrochloride was removed by rinsing, reduced pressure deliquoring was carried out, it recrystallized from ethanol 300ml, and 504g (84% of yield) of white solid-states was obtained.

[0095] Other sample compounds as well as the above-mentioned synthetic example were obtained.

[0096] [Example 1] The compound of a publication was fully mixed to Table 1, and it applied so that a knife coating machine might be used and the thickness after desiccation might be set to 30 micrometers on a surface treatment aluminum plate. After carrying out heat desiccation for 5 minutes at 80 degrees C, it baked for 30 minutes at 150 more degrees C, and the hardened material was obtained. About the obtained hardened material, fire retardancy was evaluated based on glass transition temperature (Tg), tensile strength, a modulus of elasticity in tension, \*\*\*\* elongation, and UL-94. A result is shown in Table 1 and 2. However, loadings are adjusted so that the Lynn content of the epoxy resin constituent obtained may become 2.0 % of the weight, the loadings of a sample compound and a comparison flame retarder are combination as solid content except a solvent, and all units are the weight sections.

[0097] Glass transition temperature was measured by the dynamic viscoelasticity method.

[0098] As a tension test, it measured by JIS-K6911.

[0099]

[Table 1]

	実施例					
	1-1	1-2	1-3	1-4	1-5	1-6
エポキシ樹脂1 <sup>*1</sup>	40	40	40	40	40	40
エポキシ樹脂2 <sup>*2</sup>	20	20	20	20	20	20
DCA <sup>*3</sup>	40	40	40	40	40	40
化合物No. 3	40.0					
化合物No. 7		43.2				
化合物No. 11			44.4			
化合物No. 13				37.4		37.4
化合物No. 15					36.5	
化合物No. 6						
ノボラック1 <sup>*4</sup>	18.8	25.9	25.8	26.1	26.2	26.1
ノボラック2 <sup>*5</sup>	18.8	25.9	25.8	26.1	26.2	26.1
溶媒 <sup>*6</sup>	80	80	80	80	80	80
反応触媒 <sup>*7</sup>	3.5	3.5	3.5	3.5	3.5	3.5
水酸化アルミニウム						15
水酸化マグネシウム						15
シリカ						20
ガラス転移温度 (°C)	179	175	178	175	200	177
引張強度 (MPa)	85	80	80	83	90	85
引張弾性率 (GPa)	2.5	2.1	2.0	2.3	2.9	2.1
引張伸び (%)	13	15	15	18	10	13
難燃性	VO	VO	VO	VO	VO	VO

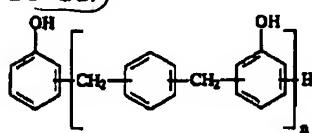
\* 1 : ビスフェノールA型エポキシ樹脂

\* 2 : カルボン酸変性NBRのビスフェノールAジグリシジルエーテル付加物

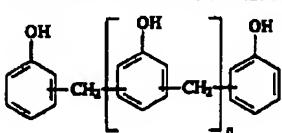
\* 3 : 2, 2-ビス(3, 4-エポキシクロヘキシル)プロパン

\* 4 : フェノール・ベンゼン・ホルムアルデヒド総合物 (三井化学(株) 製) (X)

LC-LL



\* 5 : フェノールノボラック (住友デュレズ(株) 製: PR-53194)



\* 6 : エチレングリコールブチルエーテルアセテート

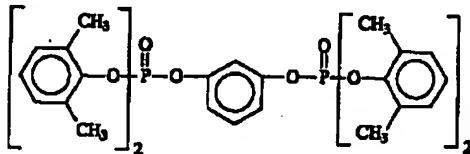
\* 7 : 2-エチル-4-メチルイミダゾール

[0100]

[Table 2]

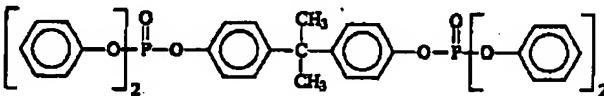
	比 較 例			
	1-1	1-2	1-3	1-4
エポキシ樹脂1 <sup>*1</sup>	40	40	40	40
エポキシ樹脂2 <sup>*2</sup>	20	20	20	20
DCA <sup>*3</sup>	40	40	40	40
比較遮燃剤1 <sup>*8</sup>	49.0			
比較遮燃剤2 <sup>*9</sup>		46.0		
比較遮燃剤3 <sup>*10</sup>			49.5	
比較遮燃剤4 <sup>*11</sup>				88.6
ノボラック1 <sup>*4</sup>	34.3	34.3	34.3	26.2
ノボラック2 <sup>*5</sup>	34.3	34.3	34.3	26.2
磨媒 <sup>*6</sup>	80	80	80	80
反応触媒 <sup>*7</sup>	3.5	3.5	3.5	3.5
水酸化アルミニウム				
水酸化マグネシウム				
シリカ				
ガラス転移温度(℃)	140	138	143	210
引張強度(MPa)	65	60	65	50
引張弾性率(GPa)	1.9	1.8	1.9	3.1
引張伸び(%)	5.5	3.8	4.8	0.8
難燃性	VO	VO	VO	VO

\* 8 :

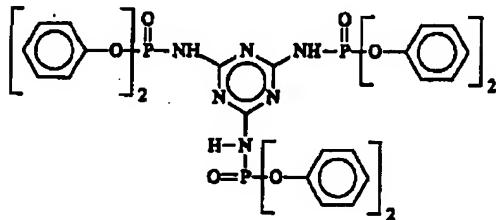


\* 9 : トリフェニルホスフェイト

\* 10 :



\* 11 :



[0101]

[Effect of the Invention] As stated above, according to this invention, the fire retardancy which was excellent without containing a halogen is shown, moreover it has a high glass transition temperature, and the epoxy resin constituent excellent in mechanical strength is offered.

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[Translation done.]

## \* NOTICES \*

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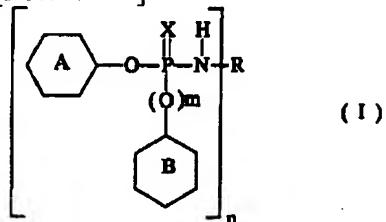
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

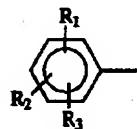
## [Claim(s)]

[Claim 1] The fire-resistant epoxy resin constituent which had the phosphoric-acid amide compound expressed with the following general formula (I) added.

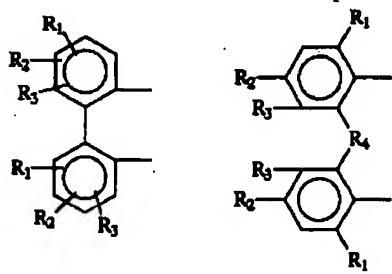
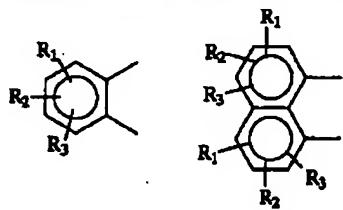
## [Formula 1]



(式中、環A及び環Bは各々独立に



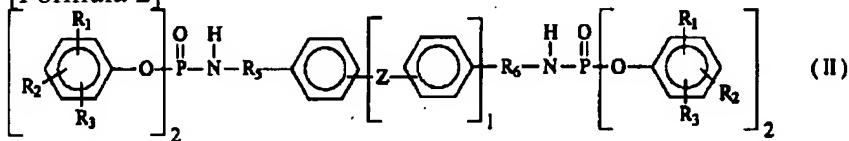
(R<sub>1</sub>、R<sub>2</sub>及びR<sub>3</sub>は各々独立に水素原子、ヒドロキシ基、ヒドロキシカルボニル基または炭素原子数1～5のアルキル基を表す)を表すか、組み合わされて



(R<sub>1</sub>、R<sub>2</sub>及びR<sub>3</sub>は各々独立に水素原子、ヒドロキシ基、ヒドロキシカルボニル基又は炭素原子数1～5のアルキル基を、R<sub>4</sub>は炭素原子数1～4のアルキリデン基を表す)を表し、Xは酸素原子又は硫黄原子を、mは0又は1を、nは1～3の数を、Rは1級アミノ基を1個又は2個有する基及びメラミンを除く1級アミノ基を3個有する基の残基を表す)

[Claim 2] The fire-resistant epoxy resin constituent according to claim 1 whose above-mentioned phosphoric-acid amide compound is a compound expressed with the following general formula (II).

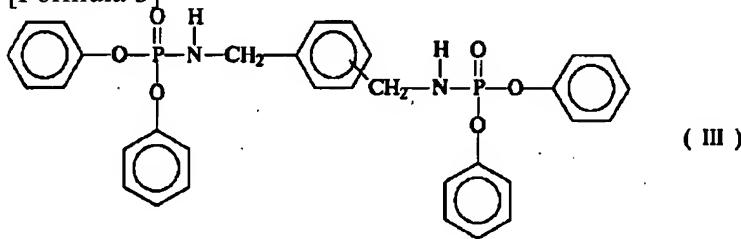
[Formula 2]



(the inside of a formula, R1, R2, and R3 -- each -- independent -- a hydrogen atom, a hydroxy group, a hydroxy carbonyl group, or the alkyl group of the carbon atomic numbers 1-5 -- R5 and R6 -- each -- independently, Z expresses the alkylidene radical of direct coupling, an oxygen atom, a sulfur atom, a sulfonyl group, an ester bond, amide association, and the carbon atomic numbers 1-4, or the condensation of a ring, and l expresses the number of 0 or 1 for the alkylene group of direct coupling or the carbon atomic numbers 1-4)

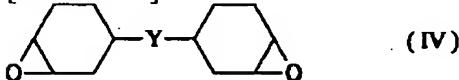
[Claim 3] The fire-resistant epoxy resin constituent according to claim 2 whose above-mentioned phosphoric-acid amide compound is the following compound (III).

[Formula 3]



[Claim 4] The fire-resistant epoxy resin constituent containing the compound in which an epoxy resin is shown by the following general formula (IV) according to claim 1, 2, or 3.

[Formula 4]



(Y expresses the alkylene group or alkylidene radical of the carbon atomic numbers 1-8 among a formula)

[Claim 5] A silica, rubber, the fire-resistant epoxy resin constituent according to claim 1 that had the phenol novolak mold-curing agent added.

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[Translation done.]